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Characterization of Electrospun Nanofibers of Cellulose Nanowhisker/Polyvinyl Alcohol Composites*1

Mijung Cho*2, Byung Dae Park*2†, and John F. Kadla*3

ABSTRACT

Cellulose nanowhisker (CNW) isolated from hardwood bleached kraft pulp (HW-BKP) using sulfuric acid hydrolysis was suspended in polyvinyl alcohol (PVA) and electrospun into composites nanofibers. Transmission electron microscopy (TEM) revealed the CNW to be rod-like, approximately of 16.1 ± 4.6 nm wide and 194 ± 61 nm long, providing an aspect ratio of about 12, with a particle size distribution range of 662.2 ± 301.2 nm. Uniform and high quality CNW/PVA composite nanofibers were successfully manufactured by the electrospinning method. As the CNW loading increases, the viscosity of CNW/PVA solutions shows a minimum at 1% CNW level which subsequently results in the smallest diameter (193 nm) of electrospun nanofibers. The average diameter of the nanofibers increased up to 284 nm with increasing CNW loading. These results suggest that the electrospinning method provides a great potential of manufacturing consistent and reliable nanofibers from CNW/PVA solution for the formation of scaffolds with potentials in future application.

Keywords : cellulose nanowhisker, electrospinning, nanofibers, polyvinyl alcohol, fiber diameter

1. INTRODUCTION

Cellulose has been used to reinforce polymer matrices in composites due to the environmental concern of other reinforcement material such as carbon fibers or glass fibers. It is the most abundant, renewable and biodegradable natural polymer on earth. In nature, cellulose exists as microfibrils of varying dimensions. These are aggregates of parallel chains of cellulose macromolecules, held together by hydrogen bonding (Hamad, 2002). The crystalline region of cellulose contributes to the mechanical strength of cellulose. Thus, it has a high structural strength and stiffness. Because of these good mechanical properties, cellulose nanowhisker (CNW), have generated a great deal of interest as a source for nanometer size reinforcement (Eichhorn *et al*., 2010).

The first study on CNW was reported by Rånby in 1952, followed by Marchessault *et al*. (1959). However, the use of nanocelluloses as a reinforcement material in nanocomposites had only started 15 years ago (Favier *et al*., 1995).

*1 Received on December 9, 2011; accepted on March 24, 2012
*2 Department of Wood Science and Technology, Kyungpook National University, Daegu 702-701, Korea
*3 Department of Wood Science, University of British Columbia, Vancouver, B.C., V6T 1Z4, Canada
† Corresponding author : Byung Dae Park (e-mail: byungdae@knu.ac.kr)

These studies demonstrated a small amount of tunicin whisker significantly enhanced the mechanical property of synthetic latex. Such work played a prominent role in generating early excitement about the potential of using nanocomposites. Therefore, in addition to its environmental friendliness, CNW can be used to fabricate new materials with remarkably improved mechanical and physical properties at lower volume fraction than existing reinforcement materials such as glass fiber, carbon fiber and carbon nanotubes (CNT). Recently, Eichhorn *et al*. (2010) published a comprehensive review on current research activities on CNW based nanocomposites and their applications. It included CNW reinforced elastomers, interfacial micromechanics of CNW based nanocomposites, hydrogen bonding exploitation of CNW, shape memory nanocomposites, or analysis of CNW dispersion etc. There are several potential applications of CNW-based nanocomposites including as a filler for adhesives, transparent layer for electronic devices, semi-structural uses, CNW/DNA hybrid nanomaterials, CNW-based biofoams, etc.

Electrospinning is a very simple and effective method of producing nanofibers with a wide range of diameters (Huang *et al*., 2003). In this process, an electrical potential is applied between a droplet of a polymer solution, or melt, held at the end of a capillary tube and a grounded target. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected and is controlled by the electric field (Chronakis, 2005). Several factors can affect the electrospinning process: a) solution properties such as viscosity, conductivity and surface tension, b) controlled variables like hydrostatic pressure in the capillary, electric potential at the tip, and the collection screen, and c) ambient parameters including temperature, humidity, and air velocity in the electrospinning chamber (Doshi and Reneker, 1995).

The number of applications and research fields that utilize electrospun polymer nanofibers has been steadily increased. It is found in filtration systems and in medical prosthesis, mainly in grafts and vessels. Other targeted applications include tissue templates, electromagnetic shielding, composite delimitation, and liquid crystal devices. It is worth noting that most of these applications are still within the laboratory settings and have yet to be commercialized (Haung *et al*., 2003).

Electrospun fibers produced from PVA have been widely studied over the past few years. Recently, organic and inorganic based PVA hybrid nanocomposite fabricated using electropinning method has attracted great interest. Jeong *et al*. (2007) studied PVA/multi-walled carbon nanotubes (MWCNT) nanofibers and found that the dispersivity and interfacial stress were predominant factors affecting the tensile strength and thermal stability of the PVA/MWCNT nanocomposites. Other studies generated fibers by electrospinning chitosan mixtures with PVA (Charernsriwilaiwat *et al*., 2010; Li and Hsieh, 2006). Charernsriwilaiwat *et al.* (2010) concluded that the chitosan/PVA nanofiber may be suitable for use in drug delivery or tissue engineering applications because of its non-toxic and biodegradable property. However, very little work has been done to systematically examine electrospun CNW-based nanofibers. A recent study demonstrated that inclusion of CNW nanofibers significantly improved the elastic modulus of the electrospun nanofibers of CNW/PVA composites, due to the strong interactions of the hydrogen bonding network (Peresin *et al*., 2010). In this work, we characterized nanofibers of CNW/PVA composites obtained by the electrospinning method. In addition, we also characterized CNW isolated from hardwood bleached kraft pulp (HW-BKP) using sulfuric acid

hydrolysis.

2. MATERIALS and METHODS

2.1. Materials

Hardwood bleached kraft pulp (HW-BKP) was obtained from Moorim Paper Co. Ltd., Korea. Sulfuric acid (95%, DC chemical Co. Ltd., Korea) and PVA (Mw 66,000) (Duksan Pure Chemical Co., Ltd., Korea) were used as received.

2.2. Preparation of CNW

CNWs were prepared from acid hydrolysis of HW-BKP using sulfuric acid (Revol *et al*., 1992; Kvien *et al*., 2005). Sulfuric acid was added to the pulp slurry (10 g of HW-BKP in 90 g of water) to obtain sulfuric acid concentration of 57%. And the acidified pulp slurry was allowed to react for 80 min at 45°C, followed by washing with de-ionized water for 20 min at 5,000 rpm (H-500, Hanil Centrifuge Co. Ltd., Korea). The supernatant was removed and replaced with fresh deionized water, mixed and repeated until the supernatant is turbid. The suspension was then dialyzed with de-ionized water until the pH of the wash water became 4. The collected supernatant was restored in the refrigerator (4°C) until used.

2.3. Characterization of CNW

Wet particle size analysis was conducted using a laser diffraction particle size analyzer (N5/LS-13320, Beckman Coulter, USA) to measure the approximate size of the CNW. During this analysis, a 0.5 wt% CNW solution was exposed to a 25 mV helium-neon laser light source for 200 s.

TEM (H-7600, Hitachi, Japan) observations were performed at an accelerating voltage of 100 kV. The sample was diluted to a concentration of 0.5 wt% and sonicated for 20 min. Three droplets of the CNW suspension were placed on a Cu-grid coated with a thin carbon film and allowed to dry at 70°C for 10 min. To enhance the contrast for TEM, the CNW were stained by allowing the grids to float in a 3 wt% solutions of uranyl acetate for 3 min. The grids were then dried at 70°C for 10 min. The particle dimensions were measured by counting individual CNW in the TEM micrographs using image analysis software (Ver. 8.5, IMT i-solution Inc., Canada).

XRD (Rigaku D/Max-2500, Japan) was used to measure the crystallinity of the CNW isolated from the HW-BKP. Powdered samples were prepared by crushing the freeze-dried CNW. However, the HW-BKP sample retained their original shape. The samples were analyzed at ambient temperature using a CuK α-1 X-ray source with a wavelength (λ) of 1.5418 Å. The angle of incidence was varied from 5° to 30° at a step of 0.02° and scanning rate of 6 °/min. The Segal method was used to calculate the crystallinity of the sample (Segal, 1959). The sample crystallinity (X_{CR}) was determined by Eq. (1) using the height of the 200 peak (I_{200}, 2θ = 22.7°) and the lowest height between the 200 and 110 peaks (I_{AM}, 2θ = 18°). I_{200} represents both crystalline and amorphous material while I_{AM} represents only the amorphous material (Segal, 1959).

$$X_{CR}(\%) = \frac{I_{200} - I_{AM}}{I_{200}} \times 100 \quad (1)$$

Analysis using this equation assumes that the amorphous material diffracts with the same intensity at 2θ of 18° and 22.7°, and that the crystalline cellulose does not contribute to the intensity at 18° (Thygesen *et al*., 2005).

2.4. Preparation of PVA/CNW Solution

The CNW suspension was first concentrated by rotary evaporation (Rotovapor R110, BÜCHI, Switzerland) and mixed with a 10 wt% PVA solution at different CNW concentrations (1, 3, 5, and 7 wt%). The CNW/PVA suspensions were vigorously mechanically stirred at 80°C for 4 hours, followed by continued stirring until the solution reached room temperature. The final mixtures were sonicated for 10 min (Sonosmasher, Jeio Tech, Korea) at 50% power output.

2.5. Electrospining of CNW/PVA Composite Nanofibers

Nanofibers from CNW/PVA solutions were prepared by horizontal electrospinning onto a rotating aluminum foil covered drum (30 cm wide) collector. The CNWs/PVA suspension was loaded into a 10 ㎖ syringe (1010TLL 81620, Hamilton Co., USA) with a metal needle (N722. 91022 m, Hamilton Co., USA) and a flow rate of 0.5 ㎖/h was applied and controlled by a syringe pump (KDS101, KD Scientific Inc., Korea). The applied voltage was 10 kV (CPS-60K02 VIT, Chungpa Emt Co., Ltd., Korea) and the needle tip to collector distance was 15 cm. After electrospinning, the collected CNW/PVA composite nanofibers were stored in a desiccator at room temperature.

The morphology of the CNW/PVA composite nanofibers was investigated using a field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi, Japan) with an accelerating voltage of 15 kV. A small piece of nanofiber mats was fixed on carbon tape and coated with Pt/Au. The average diameter of the composite nanofibers was obtained by measuring individual fibers in the FE-SEM micrographs using image analysis software (Ver. 8.5, IMT i-solution Inc., Canada).

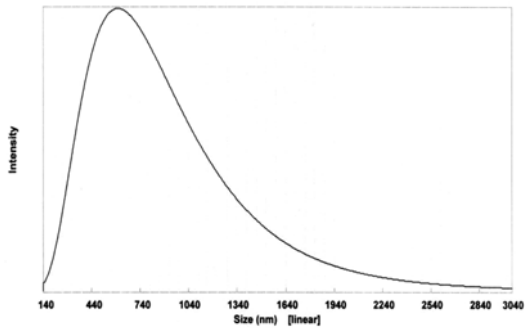

Fig. 1. Wet particle size analysis of CNW isolated from HW-BKP.

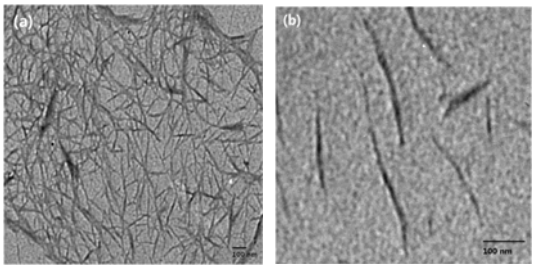

Fig. 2. TEM image of CNW isolated from HW-BKP at different magnifications: (a) × 10000, (b) × 30000.

3. RESULTS and DISCUSSION

Fig. 1 is the wet particle size distribution of CNWs obtained after sulfuric acid hydrolysis from HW-BKP. The size distribution of the CNW ranged from 140 nm to 3040 nm, which gives an average of 662.2 ± 301.2 nm, based on an analysis of more than 0.8 million particles. This method measured both width and length of the CNWs by light scattering. This average value was quite differed from the dimensions measured by TEM.

Fig. 2 is TEM images of the rod-like CNWs prepared by acid hydrolysis from HW-BKP. Analysis of the TEM images revealed that the isolated CNW had a width (d) of 16.1 ± 4.6 nm and length (L) of 194 ± 61 nm, which corre-

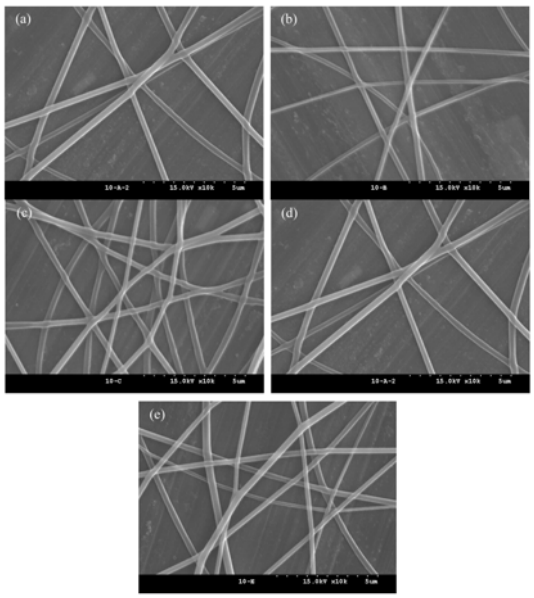

Fig. 3. FE-SEM images of electrospun nanofibers of CNW/PVA composites at different CNW concentrations. (a) 0%, (b) 1%, (c) 3%, (d) 5% and (e) 7%.

sponds to an aspect ratio (L/d) of 12. These dimensions are in agreement with those reported in previous studies (Cho and Park, 2011). However, the width was slightly larger, which was most likely due to the difference between the types of raw materials (Revol *et al*., 1992).

The crystallinity of cellulose has been used to describe the changes in cellulose structure after physicochemical and biological treatments (Thygesen *et al*., 2005). In this study, the crystallinity of CNW isolated by sulfuric acid hydrolysis was determined using the Segal method (Segal, 1959). The crystallinity of CNW isolated by sulfuric acid hydrolysis was calculated to be 83.1%, while that of the HW-BKP sample was 83.9%. This suggests that the crystallinity of CNW and HW-BKP are quite similar. This is in contrast to a previous study, which demonstrated that the crystallinity of CNW increased to 85.2% when microcrystalline cellulose (MCC)

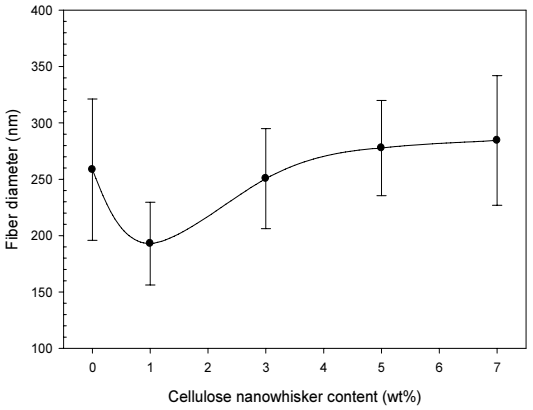

Fig. 4. Average diameters with standard deviation of the electrospun nanofibers of CNW/PVA composites as a function of CNW concentration

was used as the raw material for acid hydrolysis (Cho and Park, 2011). It is believed that the close crystallinity between the CNW and the HW-BKP was due to the difference in the sample preparation for XRD measurement; the CNW sample was in powdered form but the HW-BKP sample was in sheet form. The crystallinity of cellulose depends on various factors such as sample preparations, measuring techniques, calculation methods, or raw materials sources (Park *et al*., 2010). In addition, the Segal method used in this work gave significantly greater values when compared to other methods. For example, Sirkka *et al.* (2000) reported that the crystallinity of fully bleached kraft pulp was 47% as measured by ^{13}C NMR spectroscopy.

The morphology of the electropun CNW/PVA composite nanofibers can be seen in the FE-SEM images as shown in Fig. 3. Images (a) to (e) are micrographs of the composite nanofibers at different CNW concentrations (0～7 wt%) after electrospinning. As seen, most of the electrospun CNW/PVA composite nanofibers have smooth and uniform surfaces without beads. This result indicates that electrospinning could be used to successfully fabricate CNW

nanofibers to reinforce the PVA polymer, and suggests that CNW-based nanofiber scaffolds could be manufactured by eletrospinning.

Fig. 4 depicts the average diameters of the electrospun nanofibers of the CNW/PVA composites, as determined from the FE-SEM images. The average diameter of the electrospun CNW/PVA composite nanofibers was the highest at a 7 wt% concentration and the lowest at a 1 wt% concentration. The average diameter of the nanofibers at 5 wt% CNWs was almost same with that of PVA/CNW nanofiber at 7 wt% CNWs. Except for the 7 wt% sample, this trend was consistent with previous studies, which reported that a higher viscosity resulted in a larger fiber diameter (Hamad, 2002; Baumgarten, 1991; Doshi and Reneker, 1995).

4. CONCLUSIONS

Composites of cellulose nanowhiskers (CNW) in PVA where investigated as a potential for nanofibres. In this study, CNW isolated from hardwood bleached kraft pulp (HW-BKP) using sulfuric acid hydrolysis were characterized. In addition, the nanofibers of CNW/PVA composites obtained by the electrospinning method were also examined. It was found that the individual rod-like CNW were 16.1 ± 4.6 nm wide and 194±61 nm long, (aspect ratio ~12), with a particle size distribution range of 662.2 ± 301.2 nm based on light scattering. When combined with PVA, these composites afforded uniform and high quality nanofibers as manufactured by the electrospinning. The smallest diameter obtained was 192 nm at 1 wt% CNW, while a maximum diameter of 284 nm was afforded when using 7 wt% CNW. These results indicate that consistent and reliable nanofibers can be obtained by electrospinning CNW/PVA solutions.

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